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Chemical and biological assessment of two offshore drilling sites in the Alaskan Arctic

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A retrospective chemical and biological study was carried out in Camden Bay, Alaskan Beaufort Sea, where single exploratory oil wells were drilled at two sites more than two decades ago. Barium from discharged drilling mud was present in sediments at concentrations as high as 14%, w200 times above background, with significantly higher concentrations of Ba, but not other metals, within 250 m of the drilling site versus reference stations. Elevated concentrations of Cr, Cu, Hg and Pb were found only at two stations within 25 m of one drilling site. Concentrations of total polycyclic aromatic hydrocarbons (TPAH) were not significantly different at reference versus drilling-site stations; however, TPAH were elevated in Ba-rich layers from naturally occurring perylene in ancient formation cuttings. Infaunal biomass and species abundance were not significantly different at reference versus drilling-site stations; infauna were less diverse at drilling-site stations. Our assessment showed that discharges from single wells within large areas caused minimal long-term, adverse impacts to the benthic ecosystem.

1. Introduction

Most of the estimated undiscovered reserves of w4.5 10^{12} L (28 billion barrels) of oil and 3.5 10^{12} m^3 of gas on the Alaska Platform are believed to be buried offshore; however, all of the >2.5 10^{12} L of oil produced in the Alaskan Arctic have been extracted from land or nearshore gravel islands (Gautier et al., 2009). A keen awareness of this unrealized resource sustains and heightens interest in offshore exploration and production in Alaska. At the same time that offshore exploration for oil and gas in the Arctic is being renewed, coastal ecosystems are undergoing rapid biological changes associated with sea-ice retreat and large inputs of soil and organic carbon from coastal erosion (Post et al., 2009; Rowland et al., 2010). Environmental concerns regarding offshore drilling include potential oil spills as well as discharges of drilling mud, formation cuttings, produced water and other effluents. Future regulatory and management decisions regarding offshore discharges in the Arctic would greatly benefit from retrospective assessments of historic drilling sites. In the Alaskan Arctic, 35 exploratory oil wells were drilled at water depths of 5e50 m in Federal waters between 1982 and 2003 (MMS, 2006). We chose two of these former drilling sites, both in Camden Bay, coastal Beaufort Sea (Fig. 1), for chemical and biological study.

The discharge, fate and effects of drilling mud and cuttings in the marine environment have received considerable investigation over the past three decades, mostly from studies in the Gulf of Mexico and the North Sea (e.g., Engelhardt et al., 1989; Kingston, 1992). Contemporary issues related to discharges of water base mud (WBM) include burial of benthic communities from drilling mud and cuttings and higher sediment oxygen demand from a higher organic content in the discharged material. Common chemicals found in WBM include barite ($BaSO_4$, a weighting agent), bentonite clay (a viscosifier), various salts and organic gels (Engelhardt et al., 1989). Discharges of WBM and cuttings are not permitted in US state waters and regulations for discharges in Federal waters since 1993 include the following: no free oil or diesel fuel, Hg at <1 mg/g and Cd at <3 mg/g (dry wt.) in barite, and minimum values for the 96-h LC_{50} for suspended particles at 3% by volume for the mysid Mysidopsus bahia (USEPA, 1993).

The footprint on the seafloor from discharges of WBM typically extends <250 m from the platform at water depths <200 m and to

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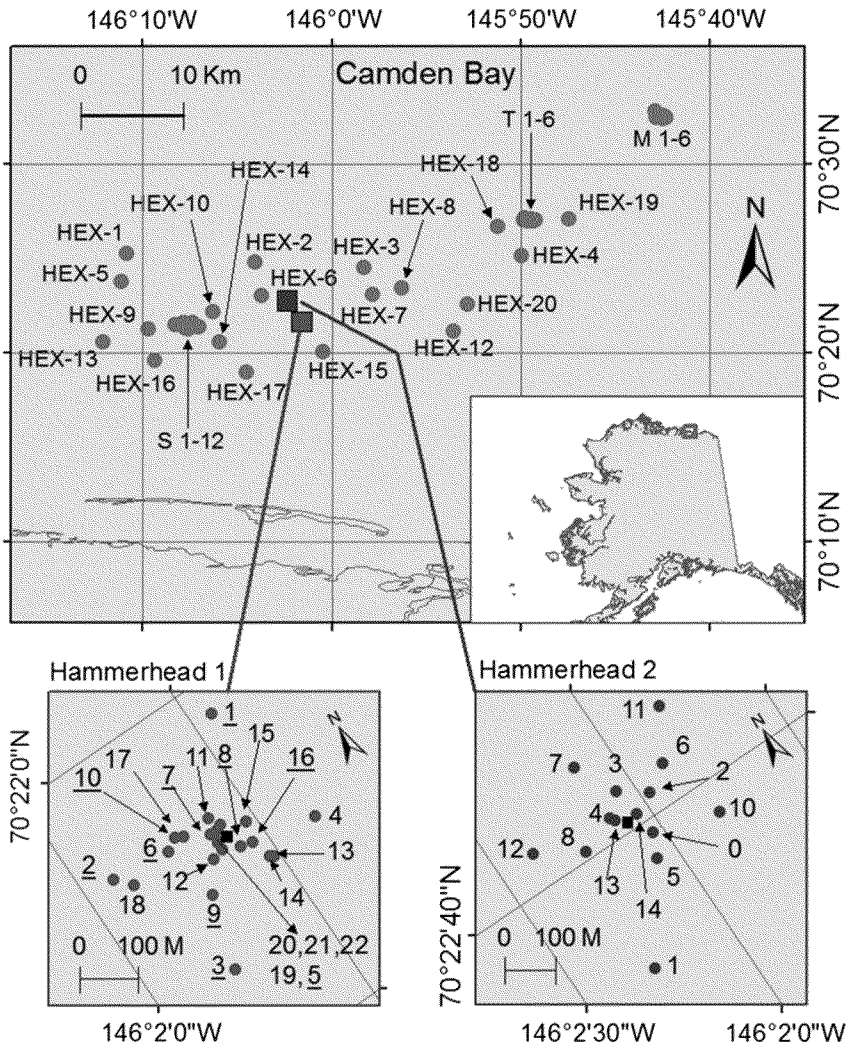

Fig. 1. Maps showing sampling stations in Camden Bay. Large map shows locations of reference stations (HEX 1e10 and 12e20, S 1e12, M 1e6, T 1e6) and Hammerhead (HH) 1 and 2 drilling sites. Smaller maps show stations within 250 m of the two drilling sites. Stations numbers for samples collected during 2008 in the HH1 area are underlined. Small rectangle on inset map shows study area in the Alaskan Arctic. Small squares on HH1 and HH2 maps show drilling sites.

distances as great as 1000 m in deeper water as a function of the volume discharged, differential settling of components, water depth, depth of discharge and current velocity (Engelhardt et al.,1989). Our observations show that thicknesses of deposits of WBM and cuttings typically range from a few centimeters to w50 cm. Ecological recovery in areas where WBM has been discharged begins soon after completion of drilling and can be well advanced within one year (Currie and Isaacs, 2005; Engelhardt et al., 1989).

Newbury (1979) predicted, prior to offshore drilling in the Beaufort Sea, that slow under-ice currents and stagnant bottom water would restrict dispersion of drilling mud. Although data for the coastal Beaufort Sea are limited, bottom water currents in our study area, Camden Bay (Fig. 1), at a water depth of w40 m are typically low (<10 cm/s) with >60% of the flow to the east (Aagard, 1984; Weingartner et al., 2005). In addition, sedimentation rates along the coastal Beaufort Sea are commonly <0.1 cm/yr (Naidu et al., 2001; Trefry et al., 2003). Therefore, low current velocities and very low sedimentation rates in our study area were expected to limit transport and burial of drilling discharges. One of very few follow-up studies of drilling discharges in the coastal Beaufort Sea, Alaska, found persistence of indicator metals (Ba, Cr, Pb, Zn) in sediments 2e4 years after drilling (Snyder-Conn et al., 1990).

The sediments of Camden Bay are silty sand and mud with >40% silt plus clay (Trefry et al., 2003) and support an infaunal assemblage dominated by polychaete worms, small mollusks and crustaceans (Carey et al., 1984; Feder and Schamel, 1976). Biota from higher trophic levels includes arctic cod, ringed seals, polar bears, sea birds and migrating bowhead whales (Frost and Lowry, 1984; George et al., 2004). Trace metals, polycyclic aromatic hydrocarbons (PAH) and other organic substances were previously found to be at background concentrations in sediments from the coastal Beaufort Sea, including nearshore areas of Camden Bay (Trefry et al., 2003; Brown et al., 2010; Naidu et al., 2012).

We investigated two exploratory oil and gas drilling sites in Camden Bay, Hammerhead 1 and 2 (Fig. 1), that were each occupied for <2 months during 1985 and 1986, respectively, to assess present-day chemical and biological conditions in the benthic environment. Our specific objectives were as follows: (1) locate persistent deposits of drilling mud and formation cuttings around the two exploratory drilling sites and (2) determine whether the present-day chemical composition and infaunal abundance and diversity of sediments within 250 m of the two drilling sites was significantly different than at adjacent reference stations.

2. Material and methods

2.1. Location and sampling

Sediments for this study were collected during August 2008 and 2009 in Camden Bay, Alaskan Beaufort Sea (Fig. 1), using the vessels Arctic Seal and Alpha Helix, respectively. During 2008, 19 random references stations across Camden Bay (identified as HEX, Fig. 1) were chosen using the hexagonal grid approach of White et al. (1992). To gain better resolution of localized variability, 12 additional random stations were chosen within 500 m of a possible future drilling site (stations S1 e12, Fig. 1) using hexagonal gridding. A third probability grid with 10 random stations was chosen within 250 m of the Hammerhead 1 (HH1) drilling site in 2008 (Fig. 1) because 250 m has commonly been an outer limit for dispersion of drilling mud and cuttings in shallow water (Trefry et al., 2007). During 2009, 12 fixed stations were occupied within 100 m of the HH1 drilling site to enhance sampling of sediments containing drilling mud (Fig. 1). In addition, 14 random stations were sampled at the HH2 drilling site using the approach of White et al. (1992). Finally, 12 additional, random reference sites were sampled during 2009 in the area of two prospective drilling sites, Torpedo (T) and Milik (M), to yield 43 reference stations at distances of 3e15 km from the two drilling sites and 22 and 14 stations, respectively, within 250 m of the HH1 and HH2 drilling sites (Fig. 1).

Sediments were collected using a pre-cleaned, double van Veen grab that obtained two side-by-side samples, each with a surface area of 0.1 m^2 and a depth of w15 cm. Sediments (top 1 cm and individual sub-surface, 1-cm thick layers) were collected from one of the two grabs and placed in separate containers for metals (polystyrene), organic substances (pre-cleaned I-Chem amber glass jars with Teflon liners) and grain size (double plastic bags). A Benthos gravity core with a 1-m long barrel, 7.5-cm diameter plastic liner, and no core catcher, was deployed into stiff sediments at several sites. Core samples were split into 0.5- to 2-cm thick layers aboard ship under clean conditions and stored in separate plastic and glass containers. All sediments samples, except those for grain size analysis, were frozen shipboard.

Invertebrates in the paired, second grab sample were washed over a 1 mm sieve and then immediately sorted, identified to the species level and preserved in 90% ethanol. Upon return to the laboratory, all preserved faunal samples were reexamined and species within each grab were blotted and weighed for wet weight biomass; shells were included in the mass measurements. No correction factor was applied for preservation effects. Biota soft tissues for stable isotope analysis were dried at 60 °C in aluminum trays aboard ship. When possible, muscle tissue for stable isotope analysis was extracted from the organism (e.g., gastropods, bivalves, large arthropods and fish). Small organisms were kept whole.

2.2. Analytical methods

Sediment samples were homogenized, completely digested in Fisher Trace Metal Grade HF, HNO_3 and $HClO_4$ and analyzed for Al, Fe, V and Zn using a PerkineElmer Model 4000 atomic absorption spectrometer, for As, Ba, Cd, Cr, Cu and Pb using a Varian Model 820-MS inductively coupled plasma mass spectrometer, and for Hg using a Laboratory Data Control Model 1235 cold vapor atomic absorption spectrometer according to our established laboratory methods (Trefry et al., 2003). Standard reference material (SRM) 2709 (soil with certified Ba value) from the National Institute of Standards and Technology (NIST) was processed with each batch of samples; concentrations of all metals were within the 95% confidence intervals for certified values. Analytical precision ranged from 1% (Al, Cu, Fe, and Pb) to 4% (Hg). Method detection limits were 25 (Cu) to >5000 (Ba, Pb) times lower than the lowest value obtained for field samples.

Extraction, isolation, and concentration of selected organic compounds from sediment samples were carried out using USEPA Method 3535. Concentrations of aliphatic hydrocarbons (C_{10} to C_{34}, plus 4 isoprenoid alkanes including pristine and phytane) were determined by high resolution, capillary gas chromatography with flame ionization detection (GC/FID, Hewlett Packard 5890 Series II). In addition to individual resolvable hydrocarbons, values for total petroleum hydrocarbons (TPH) were obtained as the sum of the total resolvable hydrocarbons plus the unresolved complex mixture from the GC/FID analysis. Concentrations of PAH (50 parent compounds plus 8 alkyl isomers) were determined by GC mass spectrometry (GC/MS, Hewlett Packard 5890 Series II) in the selected ion mode. Method detection limits were as follows: 1.4 mg/g for total petroleum hydrocarbons (TPH), 1.1 mg/g for the saturate biological markers, 0.17e1.4 ng/g for individual PAH, and 0.010e 0.014 mg/g for the n-alkanes. Results for SRM 1582 (NIST) were within 10% of certified values. Sediment organic carbon content and grain size were determined by methods described elsewhere (Trefry et al., 2003).

Sediment cores were age-dated using data for total ^{137}Cs and excess ^{210}Pb according to methods described by Kang et al. (2000); counting was carried out with a well-type Princeton Gamma Tech Model IGW11023 intrinsic germanium detector. Detector efficiency and counting accuracy were standardized using the river sediment SRM 4350B (^{137}Cs) from the NIST and RGU-1 (^{210}Pb) from the International Atomic Energy Agency.

Dried tissue samples for stable carbon isotope analysis were homogenized using a mortar and pestle, treated with 1 N HCl and rinsed with distilled water to remove carbonates, and then dried at 60 °C. Whenever possible, muscle tissue free of shell or exoskeleton was excised and not acidified. Our own analyses show no effect from acidification and rinsing on $d^{13}C$ values and no abnormal carbon isotopic signatures that required explanation were obtained. Tissues for stable nitrogen analysis were homogenized, but not acidified. All samples were analyzed using an automated system for coupled $d^{13}C$ and $d^{15}N$ that included a Finnegan MAT Delta Plus mass spectrometer linked to a CE Instruments elemental analyzer. Samples were combusted at 1020 °C and injected into the mass spectrometer via continuous flow. Results are expressed in standard d notation relative to carbonate PeeDeeBelemnite and atmospheric nitrogen standards for carbon and nitrogen, respectively. Precision was ± 0.2 &.

2.3. Statistical analysis

Statistical analyses were performed using Systat 12 and JMP 10. The apriori alpha value used to define statistical significance was set at 0.05 ($\alpha = 0.05$) for all statistical tests. Linear least squares regressions were computed to determine the relationship between individual pairs of parameters (e.g., sediment Cr versus Al, abundance versus Ba). Comparison of two independent groups of data (e.g., sediment Ba at reference versus drilling-site stations) was carried out using two-tailed t-tests. Levene's test was used to determine the equality of variance between two independent data sets and pooled variance was used for all t-tests in this study based on Levene's p values >0.05.

PRIMER (Plymouth Routines In Multivariate Ecological Research) software was used to analyze benthic biota community diversity using Pielou's, Shannone Wiener and Simpson's indices. Pielou's index for evenness was determined to measure equitability (i.e., how evenly the individuals were distributed among the different species). The Shannone Wiener diversity index was used

to explore species diversity and was calculated using the natural log of the measurements. Simpson's index reflected dominance with the largest values corresponding to assemblages where total abundance was dominated by one, or a very few, of the species present. The reciprocal of the Simpson index was used here; therefore a smaller index indicated that fewer species, of the total possible, were observed at a given station.

3. Results and discussion

3.1. Chemical assessment of sediments

Surface sediments and sediment cores were collected to search for remnant deposits of drilling mud and formation cuttings and to determine whether concentrations of metals and organic compounds in sediments from within 250 m of the HH1 and HH2 drilling sites were significantly different than at reference stations located >3 km from the drilling sites (Fig. 1). Long-term persistence of drilling deposits near the sediment surface was expected due to very low sedimentation rates of <0.1 cm/yr (i.e., <2 cm during the 20 years since drilling occurred, Trefry et al., 2003). The total amount of drilling mud plus formation cuttings discharged from single wells drilled to sub-seafloor depths of ~2449 and ~1969 m at the HH1 and HH2 sites, respectively, were calculated to have volumes of 622 and 430 m^3 (Table 1). If the mud and cuttings from the HH1 and HH2 wells were hypothetically spread out evenly at a thickness of 20 cm around each discharge point, they would cover circles with radii of ~31 and ~26 m, respectively (Table 1). Therefore, these discharges were expected to have very small footprints on the seafloor relative to the area of Camden Bay (~700 10^6 m^2).

Barium was used as a marker for drilling mud in sediments because barite ($BaSO_4$, with an extremely low solubility) made up >70% of the dry weight of drilling mud components at each site (Table 1). Industrial barite typically contains ~53% Ba (530,000 mg/g, Trefry et al., 2007). Concentrations of Ba in surface sediments (0e1 cm) were above background values of 740 mg/g (mean þ 2 SD, Table 2) at 12 of 22 stations around the HH1 drilling site, 11 stations at <100 m and one station at 100e200 m from the drilling site (Fig. 2). Barium values were >2000 mg/g at 3 stations (HH1e5, e8 and e19), including a maximum value of 69,700 mg/g (at HH1e19), ~100 times greater than background (Fig. 2). All elevated Ba concentrations (>740 mg/g) in the HH1 area, except one, were found near the center or to the east of the drilling site (Fig. 2), a trend consistent with water flow to the east >60% of the time (Aagard, 1984; Weingartner et al., 2005). At the HH2 drilling site, Ba values >740 mg/g in surface sediments (at 1100e1470 mg/g) were found at 3 of 14 stations, all located <200 m from the drilling site. Lower Ba concentrations at the HH2 drilling site were consistent with discharge of ~40% less barite at this site relative to the HH1 site (Table 1).

Sediment cores were collected at two reference stations (S2 and S8) and 20 drilling-site stations, fifteen at HH1 (1e8, 11, 15, 18e22) and five at HH2 (2, 4, 6, 8, 11) to determine the vertical distribution of drilling mud and cuttings. Barium concentrations were at uniform and background concentrations in the cores from the two reference stations and at 7 of 15 and 4 of 5 stations, respectively, from the HH1 and HH2 areas. Concentrations of Ba were greater than 2000 mg/g in only three cores (HH1e5, e8 and e19), all collected within 50 m of the HH1 drilling site.

In the most extreme case, at station HH1e19 near the center of the HH1 drilling site, concentrations of Ba increased from ~7000 mg/g at 0e1 cm to 140,000 mg/g at 18e19 cm and then decreased to background values of ~660 ± 90 mg/g at depths below 26 cm, the boundary between an upper layer containing drilling mud with natural sediment below (Fig. 3A). Barium values in the sediment core from HH1e16, just 50 m away, were at background except in the top 2 cm (Fig. 3A). The maximum Ba value in the core from station HH1e5 was 124,000 mg/g at 7e8 cm, whereas only the top 4 cm in the core from station HH1e8 contained Ba enrichment at <30% above background (i.e., 820e950 mg/g). Overall, the horizontal and vertical extent of the Ba signature supports very limited dispersion or burial of the drilling mud and cuttings as predicted by Newbury (1979) and expected by us.

Previous efforts to obtain reliable sedimentation rates and thereby place a time scale on sedimentary process along the coastal Beaufort Sea have been complicated by very low activities for ^{137}Cs and excess ^{210}Pb as well as physical and biological mixing of sediments (Naidu et al., 2001; Trefry et al., 2003). Only three of the cores from this study were reliably age dated; they yielded sedimentation rates of 0.03e0.10 cm/yr that were consistent with previous results (Naidu et al., 2001; Trefry et al., 2003). More relevant to this study, no detectable ^{137}Cs was found in the Ba-rich layer containing drilling mud and cuttings from station HH1e19; however, ^{137}Cs was detected in the top 1 cm and below 30 cm in the core (Fig. 3A and B). These observations are consistent with the expected absence of ^{137}Cs in ancient cuttings and drilling mud and the presence of ^{137}Cs in sediment deposited since 1950 when the isotope was first introduced to Earth during nuclear bomb testing. Activities of ^{137}Cs also were non-detectable in the 4e20-cm section of the core from station HH1e16 even though Ba was at background concentrations and no indication of drilling mud was detected (Fig. 3A and B). This ^{137}Cs-free layer at station HH1-16, relative to the top 4 cm and the bottom 15 cm (Fig. 3B), may contain ancient cuttings from the uppermost portion of the ~2449-m drill hole that were obtained without using drilling mud. Vertical profiles for excess ^{210}Pb confirm the observations from the ^{137}Cs data in that no excess ^{210}Pb was detected in the Ba-rich layer in the core from station HH1e19 and the apparently old sediment layer in the core from station HH1e16.

In contrast with Ba, concentrations of Al, As, Cd, Fe, Hg, Pb, V and Zn were not statistically different in surface sediments collected within 250 m of the HH1 and HH2 drilling sites relative to the reference stations (t-tests, two tailed, pooled variance, $\alpha = 0.05$,

Table 1
Primary components and amounts of drilling mud and formation, cuttings discharged during exploratory drilling at Hammerhead, 1 and 2 sites in 1985 and 1986, respectively. Calculated areas, (A) and radii (r) of deposits are based on hypothetical thickness of, 20 cm. Data courtesy of Shell Exploration and Production Company.

Component	Mass (dry) (10^6 g)	Density (dry) (g/cm^3)	Volume (dry) (10^6 cm^3)	Volume (wet) (10^6 cm^3)
Hammerhead 1				
Barite	523	4.0	131	335[a]
Bentonite clay	65	2.6	25	64[a]
Cellulose polymer	7.4	1.5	4.9	13[a]
KCl	78[b]	e	e	e
NaCl	67[b]	e	e	e
Formation cuttings	420	(2.0)[c]	e	210
Total				622
A = 622 10^6 cm^3/20 cm = 31 10^6 cm^2; r = O(3100 m^2/3.14) = 31 m				
Hammerhead 2				
Barite	295	4.0	74	189[a]
Bentonite clay	58	2.6	22	57[a]
Cellulose polymer	2.3	1.5	1.5	4[a]
Resinated lignin	2.2	1.1	2.0	5[a]
Xanthan polymer	1.3	0.7	1.9	5[a]
Formation cuttings	340	(2.0)[c]	e	170
Total				430
A = 430 10^6 cm^3/20 cm = 22 10^6 cm^2; r = O(2200 m^2/3.14) = 26 m				

[a] Sediment water content including drilling mud was 61% by volume.
[b] In solution, not included in volume.
[c] Wet density.

Table 2
Summary data for metals in surface sediments from reference stations, within 250 m of the Hammerhead 1 and 2 (HH1 and HH2) sites and in drilling mud used at these sites. Numbers in bold and underlined identify metals with concentrations that were statistically greater (t-test, two tailed, pooled variance, a ¼ 0.05) at the HH1 or HH2 drill-site stations versus the reference stations.

Area	Statistic	Al (%)	As (mg/g)	Ba (mg/g)	Cd (mg/g)	Cr (mg/g)	Cu (mg/g)	Fe (%)	Hg (mg/g)	Pb (mg/g)	V (mg/g)	Zn (mg/g)
Reference Stations (n ¼ 43)	Mean	5.77	16	630	0.21	79	21	3.01	0.046	15	126	89
	SD	0.64	3	55	0.03	9	3	0.29	0.009	2	17	10
	Median	5.87	15	638	0.20	79	22	2.97	0.045	15	128	91
	Max	7.21	22	714	0.28	96	27	3.61	0.083	18	156	108
	Min	4.23	10	456	0.14	59	14	2.27	0.027	10	87	64
HH1 (n ¼ 22)	Mean	5.69	15	**4860**[b]	0.20	**85**[c]	**24**[d]	2.97	0.048	18	124	89
	SD	0.38	3	e	0.03	14	9	0.16	0.012	10	10	7
	Median	5.79	14	794	0.20	81	22	2.93	0.046	14	127	89
	Max	6.22	21	69,700	0.29	135	58	3.39	0.096	50	138	106
	Min	4.51	10	585	0.15	73	19	2.76	0.037	13	88	75
HH2 (n ¼ 14)	Mean	5.90	15	**766**[b]	0.20	82	22	3.18	0.046	14	130	91
	SD	0.53	2	315	0.02	8	3	0.26	0.006	1	15	9
	Median	5.88	15	646	0.20	80	22	3.19	0.044	14	130	90
	Max	7.36	18	1470	0.25	103	30	3.91	0.059	18	167	116
	Min	5.01	13	477	0.18	68	19	2.75	0.039	12	105	80
Drilling Mud[a]	e	e	e	159,000	e	133	e	e	0.12	30	e	177

[a] Drilling mud data courtesy of Shell Exploration and Production Company.
[b] $p < 0.01$.
[c] p ¼ 0.038.
[d] p ¼ 0.045.

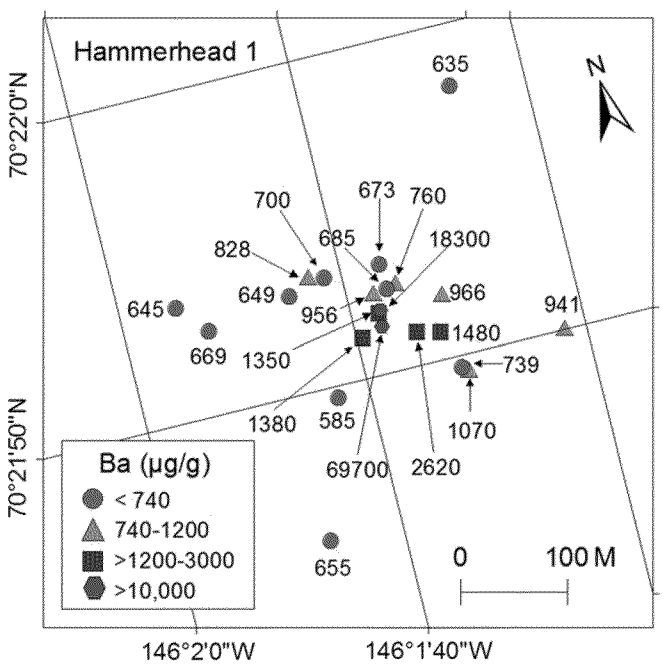

Fig. 2. Barium concentrations in surface sediments within 250 m of the Hammerhead 1 drilling site. Location of drilling site is coincident with the two hexagonal markers.

concentrations for surface sediments in Table 2). Mean concentrations of Cr and Cu were significantly higher, by 8 and 14% respectively, at the HH1 stations relative to the reference stations (concentrations for surface sediments in Table 2). The very limited number of significant differences in metal values between drilling-site and reference stations, excluding Ba, resulted from restricted dispersion of and relatively low metal concentrations in the drilling mud and cuttings (Table 2). When we compared stations within 50 m of the drilling sites (n ¼ 14) with reference stations (n ¼ 43), the results were the same as obtained for <250 m from drilling sites with Ba concentrations significantly greater at HH1 and HH2 and Cr and Cu significantly greater at HH1 relative to reference stations.

In addition to testing for significant differences in metal concentrations between reference and drilling-site stations, we also identified specific stations where concentrations of metals in surface and subsurface sediments were above background for the coastal Beaufort Sea using previously determined background concentrations as described below and in Trefry et al. (2003). Background concentrations of Al and many trace metals vary naturally as a function of sediment grain size, organic carbon content and mineralogy, with higher values in fine-grained aluminosilicates (clays) and lower values in coarse-grained quartz sand and carbonate shell fragments. Our assumption is that natural concentrations of metals, without detectable anthropogenic inputs, will be linearly correlated with Al and thus data points will plot within prediction intervals calculated from linear regression analysis as shown on metal versus Al plots (e.g., Fig. 4A, using previous baseline data for the coastal Beaufort Sea, including Camden Bay, from Trefry et al., 2003).

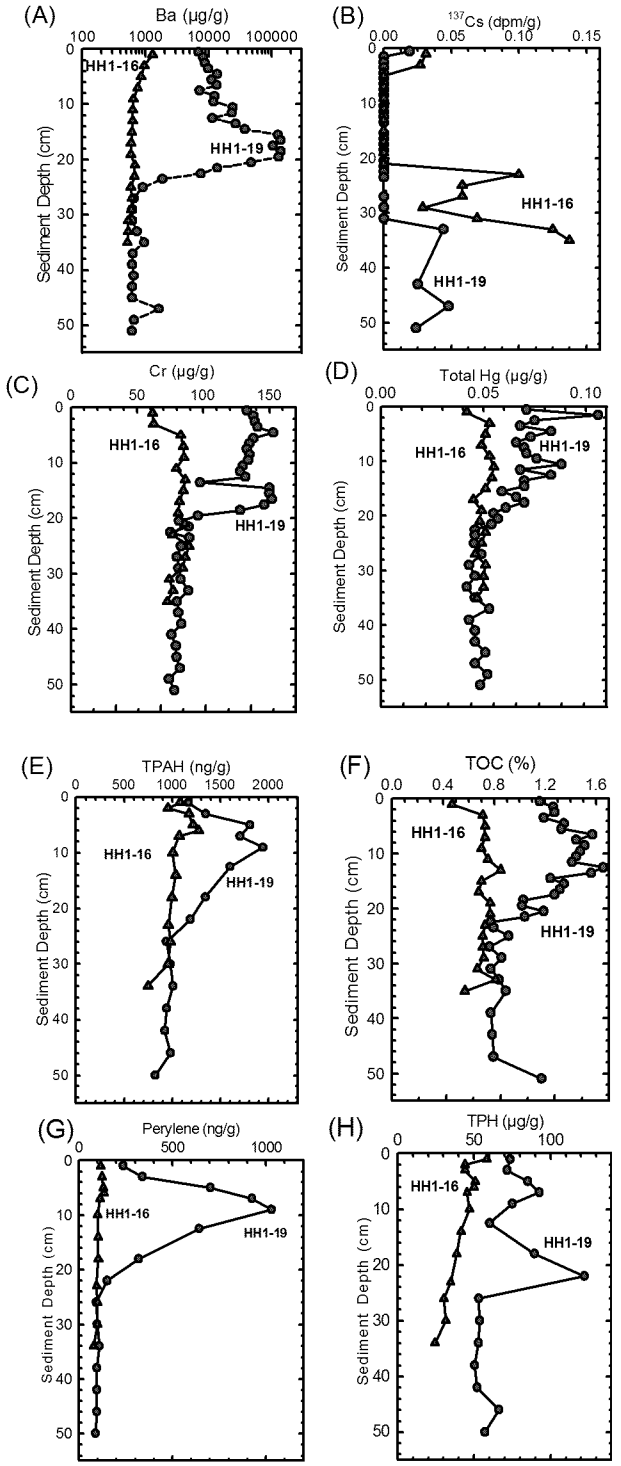

Fig. 3. Vertical profiles for sediment (A) Ba, (B) ^{137}Cs, (C) Cr, (D) total Hg, (E) total polycyclic aromatic hydrocarbons (TPAH), (F) total organic carbon (TOC), (G) perylene and (H) total petroleum hydrocarbons (TPH) for stations HH1-19 and HH1-16 near the Hammerhead 1 (HH1) drilling site.

Data from this study in Camden Bay have been plotted on metal versus Al graphs where the linear regression lines and 99% prediction intervals were prepared using background samples from the coastal Beaufort Sea, including Camden Bay (Trefry et al., 2003). For example, all data points for V in surface sediments and sediment cores from this study of Camden Bay plotted below the previously established upper prediction interval for background sediments (Fig. 4B) and thus no anthropogenic inputs of V can be linked to drilling discharges (Fig. 4B). The small gray markers on Fig. 4AeF show baseline data from Trefry et al. (2003) that were used to create the regression lines and prediction intervals for each graph. The large baseline data set with a relatively uniform distribution of points around a mean of 4% Al on the x-axis, coupled with very strong correlation coefficients, mute the commonly observed hyperbolic tendency of the prediction intervals. Trends for As, Cd and Zn follow the pattern shown for V with no evidence of anthropogenic inputs of these metals.

For Cr, two data points for surface sediments and all data points ($n = 23$) from Ba-rich layers in cores at stations HH1e19 and HH1e5 plotted above the upper prediction interval on the Cr versus Al graph (Fig. 4C). Concentrations of Cr were 60e90% higher than background values in Ba-rich layers for cores from stations HH1e19 (Fig. 3C) and HH1e5, but not in cores from any other location (e.g., station HH1e16, Fig. 3C). Chromium lignosulfonate was used to reduce viscosity and prevent flocculation in drill holes prior to the late 1980s and as much as w0.4% of the total mud mixture from this study included a lignosulfonate additive with a small, but unknown amount of Cr. The drilling mud was reported to contain Cr at 133 mg/g (Table 2), in close agreement with the average Cr value of 134 ± 15 mg/g for the top 20 cm of sediment in the HH1e19 core (Fig. 3C).

Three data points for Hg (one in surface sediments and two from cores) plotted slightly above the upper prediction interval on the Hg versus Al plot constructed using baseline data from the coastal Beaufort Sea (Fig. 4D). Two data points from the baseline data set also plotted above the upper prediction interval, consistent with a 99% prediction interval. Total Hg values were significantly higher in the top 20 cm of the HH1e19 core (0.071 ± 0.012 mg/g) than at 22e52 cm in the core (0.047 ± 0.003 mg/g; Fig. 3D); however, only two samples contained Hg at concentrations greater than the defined background for sediment from the coastal Beaufort Sea (Fig. 4D). Barite is a possible source of observed Hg enrichment; however, based on data for Hg and Ba in sediments near the HH1 drilling site, concentrations of Hg in barite used in the drilling mud were likely well below the limit for Hg of 1 mg/g in barite that was established in 1993 [e.g., calculated maximum Hg in barite = (0.066 mg Hg/g)/(14% Ba) (53% Ba in barite) = 0.25 mg/g].

Concentrations of Pb and Cu were above background in surface sediments from stations HH1e5 and HH1e19, both located within 25 m of the HH1 drilling site (Fig. 4E, F). Concentrations of Pb and Cu also were elevated by 50 and 90%, respectively, above background in the HH1e19 core (Fig. 4E and F). Possible sources of Pb and Cu include pipe thread sealant, marine paints, impurities in drilling mud components, and with sulfide minerals in formation cuttings.

No significant differences were found for concentrations of total PAH (TPAH) in surface sediments from reference stations versus stations within 250 m of each drilling site (Table 3). When data for samples within 50 m of the drilling site ($n = 10$) were used in the t-test, concentrations of TPAH were significantly higher at the HH1 drilling-site relative to reference stations ($p = 0.011$). Above background values of TPAH in surface sediments (>1260 ng/g; mean þ 2 SD, Table 3) were obtained only at stations HH1e19 (1700 ng/g) and HH1e20 (3540 ng/g), both located within 25 m of the HH1 drilling site. In the core from station HH1e19, concentrations of TPAH increased from 1180 ng/g in the top cm to a maximum of 1940 ng/g at 8e10 cm and then decreased to background values of 940 ± 60 ng/g from 24 cm to the bottom of the core (Fig. 3E). No elevated concentrations of TPAH were found in the other cores, including those from stations HH1e16 (Fig. 3E), HH1e21 and HH1e22, all located within 50 m of the HH1 drilling site.

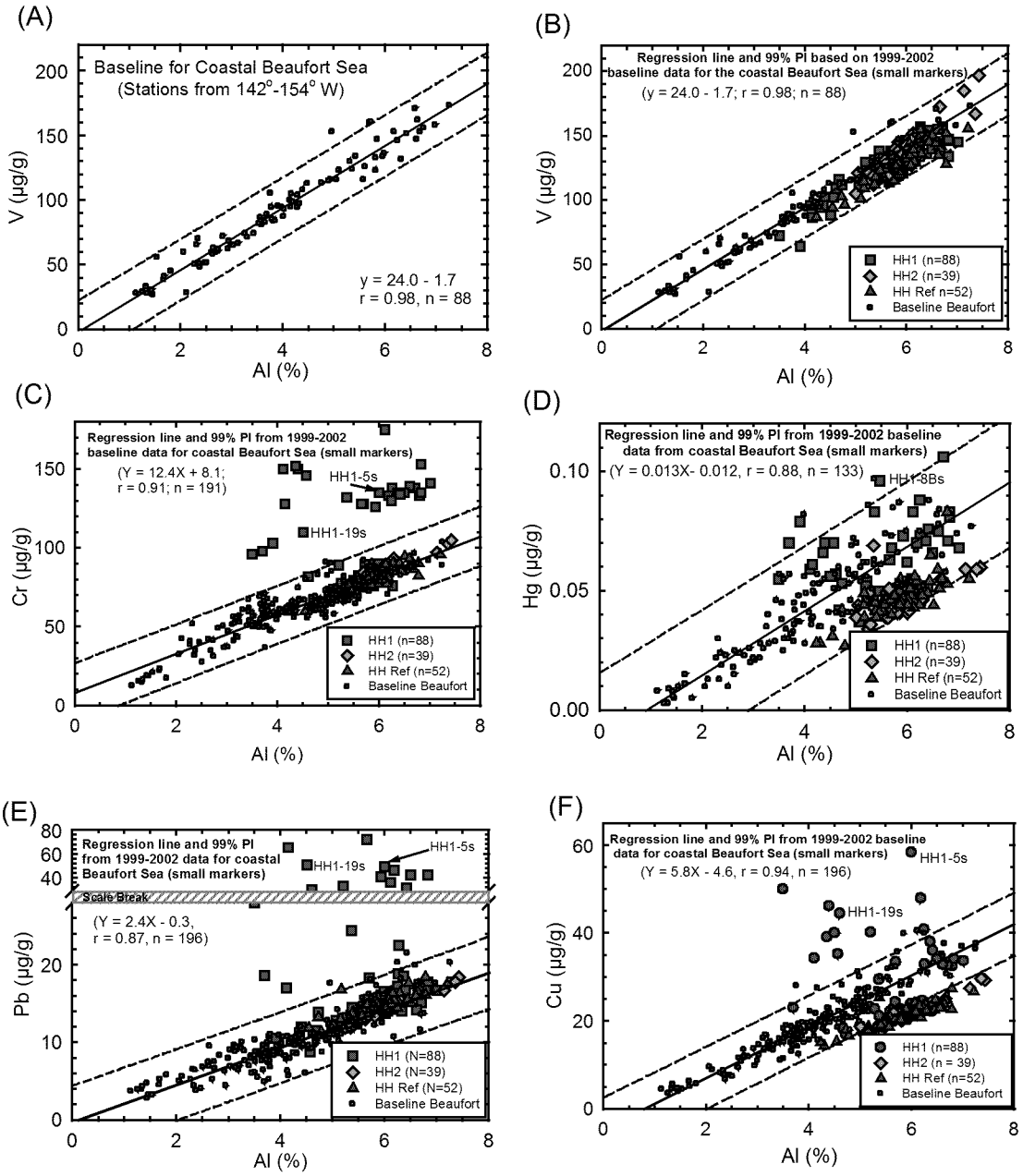

Fig. 4. (A) Concentrations of V versus Al for baseline sediments from the coastal Beaufort Sea including Camden Bay (from Trefry et al., 2003), and concentrations of (B) V versus Al, (C) Cr versus Al, (D) Hg versus Al, (E) Pb versus Al and (F) Cu versus Al for all surface sediments and sediment cores from this study in Camden Bay (HH1 and 2 ¼ Hammerhead 1 and 2 drilling sites, HH Ref corresponds with reference stations in Camden Bay). Linear regression lines, equations and 99% prediction intervals (PI) that define background concentrations are from previous baseline data (Trefry et al., 2003) for the coastal Beaufort Sea and are shown with small markers. Surface (s) sediments with above background metal values are identified by number on pertinent graphs.

Concentrations of TPAH correlated strongly with values for TOC ($r = 0.81$, $n = 17$, $p < 0.001$) in the top 24 cm of the core from station HH1e19 that contained drilling mud and cuttings as corroborated in the vertical profiles for TPAH and TOC (Fig. 3E and F). Furthermore, samples with higher concentrations of both TPAH and TOC contained higher concentrations of perylene (Fig. 3G), a naturally occurring PAH formed during long-term diagenesis of organic matter (Venkatesan, 1988). The excess TPAH in the upper portion of the core from station HH1e19, relative to background (i.e., core HH1e16, Fig. 3E) was equal to the concentrations of excess perylene (Fig. 3E, G). Higher concentrations of PAH and perylene in the top of the core from station HH1-19 were likely due to organic-rich cuttings that were drilled from the ancient sedimentary formation. Excluding perylene, concentrations of individual PAH were not significantly different at drilling-site versus reference stations (e.g., phenanthrene and benzo(a)pyrene in Table 3).

Concentrations of total petroleum hydrocarbons (TPH) were significantly higher within 250 m and 50 m of the HH1 and HH2 drilling sites than at the reference stations (concentrations in Table 3). Values above background for TPH (>65 mg/g, mean þ 2 SD) were found in surface sediments from 5 of 36 drilling-site stations (HH1e5, 18, 19, 21 and HH2e12); concentrations >100 mg/g were found only at station HH1e5 (192 mg/g). Among all cores, concentrations of TPH were above background only in the top 24 cm of

Table 3
Summary data for total polycyclic aromatic hydrocarbons (TPAH), selected individual PAH (BaP ¼ benzo(a)pyrene), total petroleum hydrocarbons (TPH), total alkanes, carbon preference index (CPI)[a], total organic carbon and silt þ clay for surface sediments from all reference stations and within 250 m of the Hammerhead (HH) 1 and 2 drilling sites. Numbers in bold and underlined identify substances, with concentrations that were statistically greater (t-test, two tailed, pooled variance, a ¼ 0.05) at the HH1 or HH2 drilling-site stations versus the reference stations.

Area	Statistic	TPAH (ng/g)	Phenanthrene (ng/g)	BaP (ng/g)	Perylene (ng/g)	TPH (mg/g)	Total alkanes (mg/g)	CPI[a]	TOC (%)	Silt þ clay (%)
Reference stations (n ¼ 43)	Mean	895	28	4	87	37	5.5	4.9	0.8	56
	SD	183	7	1	21	14	0.9	0.7	0.2	12
	Median	915	28	4	87	36	5.4	4.9	0.7	57
	Max	1310	45	6	130	63	8.8	6.6	1.3	87
	Min	484	15	2	42	12	3.3	3.7	0.5	29
HH1 (n ¼ 22)	Mean	1060	30	5	**137**[b]	**56**[b]	5.7	4.6	0.7	60
	SD	590	4	3	157	35	1.2	0.5	0.1	8
	Median	890	30	4	94	42	5.6	4.7	0.7	61
	Max	3540	37	18	773	192	8.1	5.8	0.9	78
	Min	630	23	3	68	34	3.9	3.8	0.6	40
HH2 (n ¼ 14)	Mean	978	30	4	**105**[b]	**55**[b]	5.7	4.8	0.8	63
	SD	189	6	1	22	12	0.7	0.6	0.1	12
	Median	975	31	5	106	51	5.7	4.8	0.8	64
	Max	1330	40	6	156	84	6.9	6.1	1.0	91
	Min	669	22	3	72	41	4.5	4.0	0.6	46

[a] CPI_{25e33} ¼ 0.5 [(nC_{25} þ nC_{27} þ nC_{29} þ nC_{31} þ nC_{33})/(nC_{24} þ nC_{26} þ nC_{28} þ nC_{30} þ nC_{32}) þ (nC_{25} þ nC_{27} þ nC_{29} þ nC_{31} þ nC_{33})/(nC_{26} þ nC_{28} þ nC_{30} þ nC_{32} þ nC_{34})].
[b] $p < 0.01$.

mud and cuttings at station HH1e19 with a maximum of 122 mg/g (Fig. 3H).

In contrast with TPH, concentrations of total alkanes were not significantly different between reference and drilling-site stations with averages that ranged from of 5.5e5.7 mg/g (Table 3). The degree of biogenic versus petrogenic hydrocarbons in sediments was determined using the carbon preference index (CPI, Table 3, Bray and Evans, 1961) where values of w1 indicate petrogenic hydrocarbons and values >3 are found for biogenic hydrocarbons; a mixture of petrogenic and biogenic components is present at intermediate values (1e3) for the CPI. Values for the CPI from our study were not statistically different at reference versus drilling-site stations with averages of 4.6e4.9, a maximum of w6 and a minimum of w4 (Table 3), in support of biogenic hydrocarbons with a higher plant source.

The only chromatogram with a distinct unresolved complex mixture (UCM) in the nC_{10} through nC_{30} carbon range was for surface sediments from station HH1e5 with a value for the UCM of 160 mg/g relative to an average of w18 mg/g for reference stations. The additional TPH may be due to a petroleum residue; however, the abundance of higher molecular weight hydrocarbons (>nC_{27}) suggested that this minor residue, found only at one station, was heavier than diesel oil and not Alaska crude oil, based on crude oil characterizations by Naidu et al. (2001) and Brown et al. (2010).

3.2. Benthic organisms at reference versus drilling-site stations

Infaunal abundance and biomass were quite variable throughout the study area, a reflection of benthic heterogeneity and patchiness in Camden Bay (Table 4, Fig. 5). A total of 179 benthic species were identified in Camden Bay. More than 90% of the average abundance at reference and drilling-site stations was dominated by polychaetes (>50%), bivalves (>20%) and crustaceans (>10%, especially amphipods, Fig. 5A and B). The highest abundance counts (>600/m^2) at both reference and drilling-site stations were driven by numerous tiny juvenile Cistenides hyperborea polychaetes. The maldanid polychaetes, Praxillella praetermissa and Maldane sarsi, were found in most samples, often in comparatively large numbers. Infaunal biomass at reference and drilling-site stations was dominated by bivalves (>50%) and polychaetes (>20%); the shift in biomass to favor bivalves resulted from the common practice of including shells in biomass estimates (Dunton et al., 2005). Values for both infaunal abundance and biomass at stations within 250 m of the HH1 and HH2 drilling sites were not significantly different than at the reference stations (Table 4). Furthermore, average abundance and biomass values for each of the five classes of organisms represented in Fig. 5 were not significantly different between reference and drilling-site stations.

Results for abundance and biomass at each station also were evaluated as a function of concentrations of sediment Ba, a primary tracer of drilling mud (Fig. 6). No significant correlations were found for Ba versus infaunal abundance or biomass for the references stations or within 250 m of the HH1 or HH2 drilling sites (Fig. 6A and B). Both linear and log-transformed Ba data were used in linear regression analyses with the various biological parameters for each of the three station groupings (Reference, HH1, HH2; Table 4); Pearson's r values ranged from ⌟ 0.03e0.34 with p values from 0.06 to 0.84. Spearman's r (rho) values also were calculated for biological parameters versus Ba and ranged from ⌞ 0.08 to ⌞ 0.33 with P values of 0.16e0.75. Therefore, only weak ($r < 0.4$) and non-significant relationships were found for Ba versus the biological parameters at reference and drill-site stations. Furthermore, abundance and biomass were not significantly different at drilling-site versus reference stations when only the 10 stations with sediment Ba values >1000 mg/g were used in the calculation. Nevertheless, infaunal biomass at the two HH1 stations (5 and 19) with Ba concentrations >3000 mg/g was w15% lower than the mean

Table 4
Means (⌟ standard deviations) for benthic faunal abundance, biomass, total species and biological indices for reference and, Hammerhead (HH) 1 and 2 drilling-site stations. Numbers in bold and underlined identify HH1 stations with significantly lower values than at reference stations (t-test, two tailed, pooled variance, a ¼ 0.05).

Parameter	Reference	HH1	HH2
Number of stations	43	21	12
Abundance (#/m^2)	412 ⌟ 262	354 ⌟ 250	410 ⌟ 369
Biomass (g/m^2)	42 ⌟ 31	35 ⌟ 34	58 ⌟ 70
Total species	17.6 ⌟ 5.0	15.6 ⌟ 6.1	17.2 ⌟ 5.7
Pielou's	0.61 ⌟ 0.17	0.52 ⌟ 0.20	0.57 ⌟ 0.22
Shannon e Wiener	1.03 ⌟ 0.34	**0.76**[a] ⌟ 0.38	0.91 ⌟ 0.42
Simpson	0.57 ⌟ 0.18	**0.44**[b] ⌟ 0.22	0.54 ⌟ 0.25

[a] p ¼ 0.005.
[b] p ¼ 0.012.

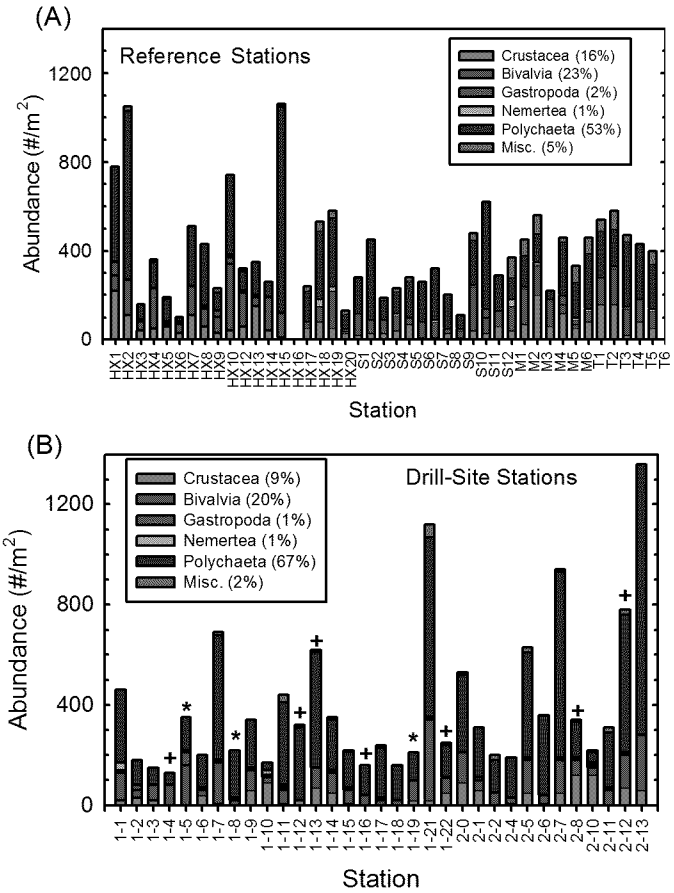

Fig. 5. Abundances of benthic fauna at (A) reference stations and (B) drilling-site stations. The HH1 and 2 stations are identified on the x-axis as 1-x and 2-x, respectively. Numbers in legend represent % of total abundance. Markers on (B) are (D) for sediment Ba at 1000e2000 mg/g and (*) for sediment Ba at >2000 mg/g.

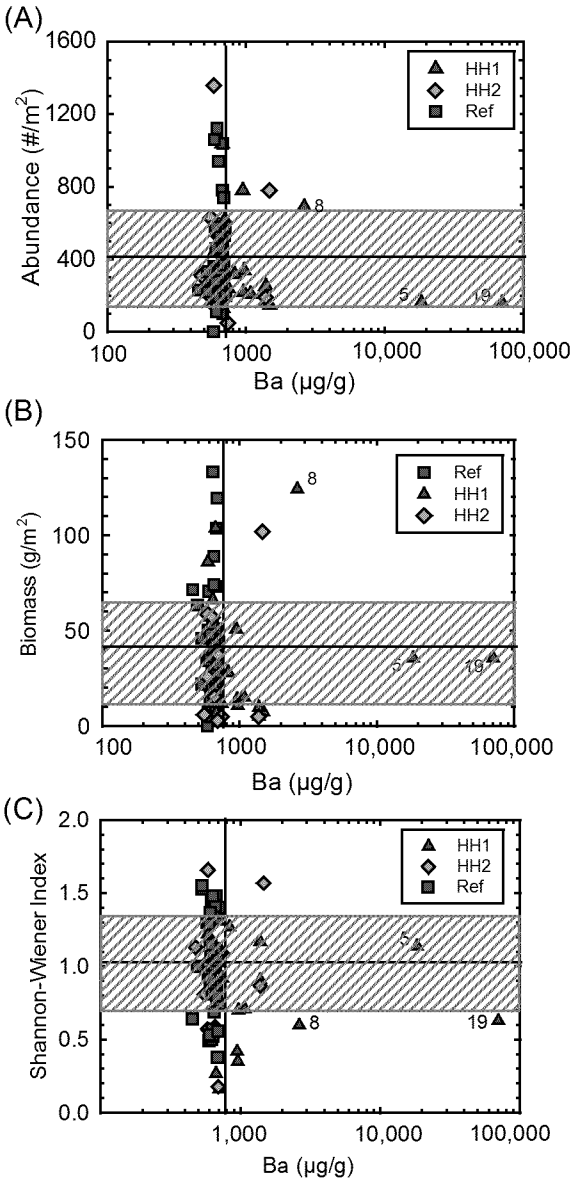

Fig. 6. Benthic faunal (A) abundance, (B) biomass and (C) values for Shannon-Wiener diversity index versus sediment Ba concentrations for reference stations and HH1 and HH2 drilling-site stations. Solid horizontal lines show means and shaded areas show ± 1 standard deviation for the parameter on the y-axis. Solid vertical lines on each graph identify background Ba values (<740 mg/g) to the left of the line. Numbers on graphs identify stations with Ba concentrations >2000 mg/g.

found at the reference stations. Infaunal abundance at these two HH1 stations (w160/m^2) was below the mean of 412/m^2 for the reference stations (Fig. 5B).

We also measured species diversity indices for benthic fauna (Table 4). Data from reference stations had the highest mean values for the three diversity categories; however, the total numbers of species were not significantly different at reference versus drilling-site stations (Table 4). Pielou's evenness index showed no significant difference for reference stations versus stations at the HH1 and HH2 drilling sites (Table 4). In contrast, values for the Shannon-Wiener diversity index and Simpson's dominance index were significantly lower at the HH1 stations than at reference stations (Table 4) indicating that fewer species of the total possible were found on average at stations in the HH1 area. As previously summarized with the discussion of abundance and biomass, no significant correlations were found for the Shannon-Wiener index versus sediment Ba (Fig. 6C). Infaunal communities at the HH1 drilling site appeared to be less diverse and were dominated by fewer species than at the reference stations. Cumaceans, various polychaetes (e.g., Heteromastus filiformis, Terebellides stroemi) and amphipods (e.g., Byblis gaimardi, Protomedeia fasciata) were not found at the drilling sites, but were found at the reference stations. These results may indicate that infaunal communities around the HH1 drilling site have been successful at repopulating the benthos but may not have fully matured following the physical disturbances from drilling.

Values for $d^{15}N$ and $d^{13}C$ were obtained for all species collected from reference and drilling-site stations. We hypothesized that long-term impacts to benthic community function and structure would result in a change in dependence on ultimate carbon sources or shifts in trophic structure as dictated by $d^{13}C$ and $d^{15}N$ values. Values for $d^{15}N$ ranged from 7.2 to 14.0‰ and defined three trophic levels using our base value for particulate organic matter (POM) of 5.5‰; these $d^{15}N$ values are compatible with those obtained by Naidu et al. (2000). Identification of three trophic levels is based on $d^{15}N$ enrichments of w3‰ per level compared to about 1‰ for $d^{13}C$ (e.g., Hobson and Welch, 1992; Dunton, 2001). Our $d^{15}N$ analyses showed that benthic organisms at higher trophic levels included predatory priapulids, anemones, and nemerteans ($d^{15}N$ ¼ 12.5e13.2‰) whereas lower trophic level biota ($d^{15}N$ ¼ 6e9‰) included suspension feeding crustaceans (amphipods and cumaceans), bivalves and bryozoans. As noted by Dunton et al. (2012) for this area of Camden Bay, the predominance of $d^{15}N$ values >6‰

indicated that POM derived from marine sources ($\delta^{15}N$ ¼ 5e7 &) was likely the major source of organic nitrogen to marine food webs in the area rather than terrestrial sources that are characterized by $\delta^{15}N$ values of 0e1.5 &.

No significant differences were found for $\delta^{15}N$ and $\delta^{13}C$ in the same organisms collected at reference versus drilling-site stations with the exception of $\delta^{13}C$ in the amphipods Haploops sp. (p ¼ 0.033, Fig. 7). Based on the diversity and stable isotope results, the drilling-site stations were characterized by having lower diversity than reference stations; however, this difference was not sufficient to produce changes in overall trophic relationships among the consumers.

4. Summary, implications and conclusions

Two historic drilling sites in Camden Bay contained deposits of drilling mud and cuttings that extended <200 m from the discharge sites and were chemically and spatially consistent with drilling records and predicted dispersion and burial patterns. Very little new sediment cover (<2 cm) was deposited since drilling due to low sedimentation rates. Concentrations of Ba and TPH were significantly higher within 250 m of both drilling sites relative to reference stations. Chromium and Cu concentrations were significantly higher (by w50%) at stations within 250 m of only the HH1 drilling site relative to reference stations. No significant differences were found for concentrations of As, Cd, Hg, Pb, V, Zn, TOC, TPAH and individual PAH (excluding naturally occurring perylene) at reference versus drilling-site stations.

Concentrations of TPAH, Cd, Hg, Pb and Zn were below the lowest value (Effects Range Low, ERL ¼ 10th percentile from an ordered list of concentrations of substances in sediments that are linked to a biological effect) for sediment quality guidelines with the exception of one Pb concentration (50 mg/g versus 47 mg/g for ERL) (Long et al., 1995; Field et al., 2002). Several authors have noted that the sediment quality guidelines should be used cautiously with an appropriate understanding of their limitations. For example, O'Connor (2004), stated that the ERL is a concentration at the low end of a continuum that relates chemistry with toxicity and that the utility of the sediment quality criteria is to call attention to a specific site where additional study, such as determining benthic biomass and community structure, may be warranted. The application of ERLs and ERMs to the sediment data from this study is presented here with these caveats. In addition, there are difficulties with values for the ERL for Cr and Cu because the ERL concentrations are lower than concentrations in typical continental crust (O'Connor, 2004). No sediment quality guidelines are available for barite in sediments; however, a limited number of studies have investigated possible impacts. For example, Starczak et al. (1992) found no significant differences in the growth rates for the pioneering polychaete species, Mediomastus ambiseta, between natural sediments and sediments containing 10% barite (Ba w50,000 mg/g). Barium values >50,000 mg/g in Camden Bay were only found within 25 m of the HH1 drilling site.

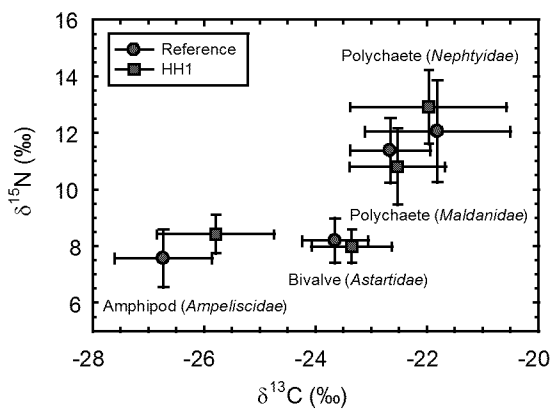

Fig. 7. Values for $\delta^{15}N$ versus $\delta^{13}C$ for specific organisms from reference (R) and HH1 drilling-site stations (D) including the following: Amphipods, Family Ampeliscidae, n_R ¼ 15, n_D ¼ 7; Bivalves, Family Astartidae, n_R ¼ 11, n_D ¼ 12; Polychaetes, Family Maldanidae, n_R ¼ 36, n_D ¼ 11; Polychaetes, Family Nephtyidae, n_R ¼ 25, n_D ¼ 16).

Measurements of infaunal community structure suggest that although invertebrates have successfully repopulated small areas of the seabed disturbed from drilling activities, succession to a more diverse faunal assemblage is still progressing, particularly around the HH1 drilling site. With this exception, our overall assessment demonstrates that discharges from single wells within the large spatial area of Camden Bay did not cause discernible long-term adverse impacts to the benthic ecosystem. When exploratory drilling transitions to production drilling, the number of wells drilled at a given site can number 10e30, or more. In the Alaskan Arctic, future plans call for downhole discharge of drilling mud after 3e4 wells have been drilled. Based on our study, decisions about future discharges should consider the volume and composition of the drilling mud and cuttings as well as the spatial distribution of drilling sites in a given geographical region.

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